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(54) Title: FOAMING SYSTEM AND DETERGENT COMPOSITIONS CONTAINING THE SAME		
(57) Abstract A controlled foaming system especially adapted for use in detergent compositions contains a foaming component capable of providing foaming or sudsing without agitation, and a delayed-release foam suppressing component. Preferably, the delayed-release foam suppressing component is releasably incorporated in a carrier, thereby delaying the release of the foam suppressing agent. Detergent compositions containing the controlled foaming system are also disclosed.		

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FOAMING SYSTEM AND DETERGENT COMPOSITIONS
CONTAINING THE SAME

5

FIELD

10 This invention relates to a novel foaming system useful in a detergent composition. More particularly, the present invention relates to granular detergent compositions intended for cleaning fabrics containing novel foaming components.

BACKGROUND

15 Foam or suds formation is desired in various applications, such as during the wash process. In detergent compositions, specific surfactants are known to provide sudsing in the wash water. Not only is the formation of foaming or sudsing desirable, but there is also a desire to readily create foam as well as maintaining the foam for a desired duration. For example, it may be desired that
20 the foam occurs immediately upon contact of a detergent composition with water. Although there are various reasons as to why foam formation is desired, one known reason is that consumers who use detergent compositions directly associate the formation of foam with the cleaning ability of the detergent composition.

25 Although the formation of foam is desired, foam may also pose problems during the washing process. For example, drainage of the suds or foam during the washing process may be difficult. Particularly for a machine wash process, the suds or foam may hamper the drainage of the wash solution from the machine before the rinse stage. Therefore, it is desired to gradually suppress
30 the formation of foam over time.

Accordingly, there is a need to produce foaming or sudsing early in the wash process, such as when the detergent composition first comes into contact with water, as well as a foam suppressing component to control the foam after formation.

None of the existing art provides all of the advantages and benefits of the present invention.

SUMMARY

5 This need is met by the present invention which is directed to a controlled foaming system especially adapted for use in detergent compositions containing a foaming component capable of providing foaming or sudsing without agitation, and a delayed-release foam suppressing component. The present invention also relates to detergent compositions containing the controlled foaming system.

10 These and other features, aspects, and advantages of the present invention will become evident to those skilled in the art from a reading of the present disclosure and the appended claims.

DETAILED DESCRIPTION

15 While this specification concludes with claims distinctly pointing out and particularly claiming that which is regarded as the invention, it is believed that the invention can be better understood through a careful reading of the following detailed description of the invention. In this specification, all percentages, ratios, and proportions are by weight, all temperatures are expressed in degrees Celsius, molecular weights are in weight average, and the decimal is represented by the point (.), unless otherwise indicated. All documents cited are incorporated
20 herein by reference. Citation of any reference is not an admission regarding any determination as to its availability as prior art to the claimed invention.

As used herein, "comprising" means that other steps and other ingredients which do not affect the end result can be added. This term encompasses the terms "consisting of" and "consisting essentially of".

25 As used herein, the term "alkyl" means a hydrocarbyl moiety which is straight or branched, saturated or unsaturated. Unless otherwise specified, alkyl moieties are preferably saturated or unsaturated with double bonds, preferably with one or two double bonds. Included in the term "alkyl" is the alkyl portion of acyl groups.

30 The present invention is directed to a controlled foaming system especially adapted for use in detergent compositions containing a foaming component capable of providing foaming or sudsing without agitation, and a delayed-release foam suppressing component. Preferably, the delayed-release foam suppressing component is a silicone foam suppressing agent which is

releasably incorporated in a carrier, thereby delaying the release of the silicone foam suppressing agent.

When the controlled foaming system first comes into contact with water, the foaming component generates rapid and stable foaming without agitation.

5 When used herein, the term "foaming" means any form of formation of gas bubbles, including sudsing and effervescing. Agitation is not necessary, but may enhance the generation of foam, and thus, may be preferred. Preferably, the foaming component produces upon contact with water, gas bubbles having an average bubble particle size of about 400 microns or less, preferably about 200
10 microns or less, and more preferably about 100 microns or less.

After the formation of foam, the delayed-release foam suppressing component is released over time and the foaming is suppressed or otherwise controlled by decreasing the amount of foam. Depending on when the foam should be suppressed, the time delay may be adjusted by choosing the
15 appropriate type of foam suppressing component. For example, for some machine wash conditions, the foam suppressing component reduces the water gas bubbles as early as upon agitation, so that preferably after about 120 seconds, the bubbles have been reduced at least about 30%. Also for example in some other machine wash conditions, after from about 360 seconds to about
20 600 seconds, the bubbles have been reduced to from about 40 to about 70% percentage, or otherwise become substantially suppressed before the rinse stage.

Preferably for hand wash conditions, the foam suppressing component may not reduce the water gas bubbles at the initial stages in the wash, since it
25 may be preferable to maintain the amount of foam for a longer period of time.

In one preferred embodiment, the foaming component and the delayed-release foam suppressing component are independent dry particles. The term "dry" is to be understood that the particles of the raw materials are substantially free of water, i.e., that no water has been added other than the moisture of the
30 raw materials themselves. Typically, the level of water is below about 5% by weight of the total particle, preferably below about 3% and more preferably below about 1.5%.

For example in a detergent composition, such as a granular detergent composition, the final composition contains a mixture of the two types of particles
35 in addition to other conventional deterative components. In another preferred

embodiment one of the particles is present as a part of an other conventional
detergent component. Having separate particles is particularly useful because
one can control the different levels and thus provide controlled delivery of the
foaming component and the suppressing component to the washing process,
5 e.g., both a more efficient and a time delivery can be achieved, to provide
optimum performance.

Although not wanting to be limited by theory, it is believed that a detergent
composition having a controlled foaming system, especially in the early phases
of the wash cycle, has cleaning benefits. For example, it is believed that the
10 foam helps transfer the surfactant in the detergent composition onto the soil to
be removed and/or on to the fabric. In addition, it is believed that the foam helps
further wetting and dissolution of the detergent composition. Furthermore, the
foam is believed to provide an early reservoir of unprecipitated surfactant to wet
fabrics and helps suspend the soil in the wash solution.

15 The controlled foaming system also is storage stable. For example, the
components do not degrade during storage while being exposed to moisture
from the air. In addition, because the foaming component contains an
effervescent granule, the incorporation of the controlled foaming system in a
detergent composition improves the dissolution characteristics of the active
20 ingredients present in the detergent composition.

Another advantage of the present invention is the improved dispensing
characteristics associated to the detergent compositions of the present invention,
e.g., the detergent compositions intended for use in a drum-type fabric washing
machine. Indeed, a difficulty with conventional high density granular detergent
25 compositions is that they are not easily flushed from the dispenser drawer of a
washing machine: i.e. when the granular composition is wetted by the water
flowing through the dispenser, the detergent ingredients may become stuck
together resulting in considerable residues of wetted and adhering powder left
behind the drawer. Similar problems are encountered when using such granular
30 detergent compositions in a dosing device in the washing drum. The presence of
the effervescent granule in the granular detergent compositions provides
improved dispensing typically when used in a washing machine and good
storage stability in respect of the dispensing potential.

The detergent compositions containing the controlled foaming system are
35 preferably solid laundry or dish washing compositions, preferably in the form of

granules, extrudates, or tablets. Preferably, granular detergent compositions have a density of at least about 500 g/l, more preferably at least about 700 g/l. The detergent compositions as well as the foaming component and the delayed-release foam suppressing component may also comprise additional ingredients, as described herein. The precise nature of these additional ingredients, and levels of incorporation thereof will depend on the application of the component or composition and the physical form of the component and composition.

A. Foaming Component

The foaming component preferably contains an effervescent granule. Any effervescent granule capable of forming gas upon contact with water, known in the art, can be used. A preferred effervescent granule comprises an acid source, capable of reacting with an alkali source in the presence of water to produce a gas.

The acid source may be any organic, mineral or inorganic acid, or a derivative thereof, or a mixture thereof. Preferably the acid source comprises an organic acid. The acid source is preferably substantially anhydrous or non-hygroscopic and the acid is preferably water-soluble. It may be preferred that the acid source is overdried. Suitable acids source components include an acid or salt form of a mono or polycarboxylic acid. Such preferred acids include those selected from the group consisting of citric, malic, maleic, fumaric, aspartic, glutaric, tartaric, malonic, succinic or adipic acid, monosodium phosphate, boric acid, 3 chetoglutaric acid, citramalic acid, and mixtures thereof. Citric acid, maleic or malic acid are especially preferred.

Also preferably, the acid source provides acidic compounds which have an average particle size in the range of from about 75 microns to about 1180 microns, more preferably from about 150 microns to about 710 microns, calculated by sieving a sample of the source of acidity on a series of Tyler sieves.

The effervescent granule preferably comprises an alkali source. Any alkali source which has the capacity to react with the acid source to produce a gas may be present in the particle, including sources capable of producing nitrogen, oxygen or carbon dioxide gas. Preferred can be perhydrate bleaches and silicate material. The alkali source is preferably substantially anhydrous or non-hygroscopic. It may be preferred that the alkali source is overdried.

Preferably the produced gas is carbon dioxide, and therefore the alkali source is preferably a source of carbonate; and in particular, a carbonate salt. Examples of preferred carbonates are the alkaline earth and alkali metal carbonates, including sodium or potassium carbonate, bicarbonate and sesqui-carbonate and any mixtures thereof with ultra-fine calcium carbonate such as are disclosed in German Patent Application No. 2,321,001 published on November 15, 1973. Alkali metal percarbonate salts are also suitable sources of carbonate species, which may be present combined with one or more other carbonate sources.

The carbonate and bicarbonate preferably have an amorphous structure. The carbonate and/ or bicarbonates may be coated with coating materials. The particles of carbonate and bicarbonate can have a mean particle size of about 75 microns or greater, preferably about 150 μ m or greater, more preferably of about 250 μ m or greater, preferably about 500 μ m or greater. It may be preferred that the carbonate salt is such that fewer than about 20% (by weight) of the particles have a particle size below about 500 μ m, calculated by sieving a sample of the carbonate or bicarbonate on a series of Tyler sieves. Alternatively or in addition to the previous carbonate salt, it may be preferred that the fewer than 60% or even 25% of the particles have a particle size below 150 μ m, whilst fewer than 5% has a particle size of more than 1.18 mm, more preferably fewer than 20% have a particle size of more than 212 μ m, calculated by sieving a sample of the carbonate or bicarbonate on a series of Tyler sieves.

The molecular ratio of the acid source to the alkali source present in the particle core is preferably from about 60:1 to about 1:60, more preferably from about 20:1 to about 1:20, more preferably from about 10:1 to about 1:10, more preferably from about 5:1 to about 1:3, more preferably from about 3:1 to about 1:2, more preferably from about 2:1 to about 1:2.

In a preferred embodiment, the effervescent granule optionally contains a binder which binds the acid source with the alkali source. Preferably, the effervescent granule comprises up to about 50 % by weight of the total granule of a binder or a mixture thereof, preferably up to about 35% and more preferably up to about 20%. Suitable binders to use herein are those known to those skilled in the art and include anionic surfactants like C6-C20 alkyl or alkylaryl sulphonates or sulphates, preferably C8-C20 alkylbenzene sulphonates, cellulose derivatives such as carboxymethylcellulose and homo- or co- polymeric polycarboxylic acid

or their salts, nonionic surfactants, preferably C10-C20 alcohol ethoxylates containing from 5-100 moles of ethylene oxide per mole of alcohol and more preferably the C15-C20 primary alcohol ethoxylates containing from 20-100 moles of ethylene oxide per mole of alcohol. Of these tallow alcohol ethoxylated with 25 moles of ethylene oxide per mole of alcohol (TAE25) or 50 moles of ethylene oxide per mole of alcohol (TAE50) are preferred. Other preferred binders include the polymeric materials like polyvinylpyrrolidones with an average molecular weight of from 12 000 to 700 000 and polyethylene glycols with an average weight of from 600 to 10 000. Copolymers of maleic anhydride with ethylene, methylvinyl ether, methacrylic acid or acrylic acid are other examples of polymeric binders. Others binders further include C10-C20 mono and diglycerol ethers as well as C10-C20 fatty acids. In the embodiment of the present invention where a binder is desired C8-C20 alkylbenzene sulphonates are particularly preferred.

In another preferred embodiment, the foaming component may also contain a surface active component which reduces the water-air surface tension. The preferred surface active component has a melting point above 45°C, and is preferably selected from the group consisting of nonionic alkoxyated amides, alkyl esters of fatty acids, or alkoxyated alcohols. Especially preferred surface active components are selected from the group consisting of polyhydroxy fatty acid amides and condensation products of aliphatic alcohols with from about 1 to about 15 moles of alkylene oxide. If a surface active component is used, the weight ratio of the surface active component to the effervescent granule is preferably from about 20:1 to about 1:10.

In still another preferred embodiment, the foaming component may further include the addition of suds boosters. The suds boosters may enhance the formation of suds in conjunction with the effervescent granule. The suds booster may be part of the same particle or component as the foaming component, or the suds booster may be a separate independent particle or component.

Preferred suds boosters include amine oxide, polyethylene glycol, monoethanol amine, diethanol amine, fatty alcohol, sugar, protein, betaine, and mixtures thereof.

Suitable amine oxides include those compounds having the formula $R^3(OR^4)_xN^+(R^5)_2$ wherein R^3 is selected from an alkyl, hydroxyalkyl, acylamidopropoyl and alkyl phenyl group, or mixtures thereof, containing from 8

to 26 carbon atoms; R^4 is an alkylene or hydroxyalkylene group containing from 2 to 3 carbon atoms, or mixtures thereof; x is from 0 to 5, preferably from 0 to 3; and each R^5 is an alkyl or hydroxyalkyl group containing from 1 to 3, or a polyethylene oxide group containing from 1 to 3 ethylene oxide groups. Preferred are C₁₀-C₁₈ alkyl dimethylamine oxide, and C₁₀-18 acylamido alkyl dimethylamine oxide.

Suitable betaines are those compounds having the formula $R(R')_2N^+R^2COO^-$ wherein R is a C₆-C₁₈ hydrocarbyl group, each R^1 is typically C₁-C₃ alkyl, and R^2 is a C₁-C₅ hydrocarbyl group. Preferred betaines are C₁₂-18 dimethyl-ammonio hexanoate and the C₁₀-18 acylamidopropane (or ethane) dimethyl (or diethyl) betaines. Complex betaine surfactants are also suitable for use herein.

The foaming component may be made by conventional methods, including as part of a tableting process, extrusion process, and/or an agglomeration process. The foaming component, whether in the form of a particle or comprised in a particle, is preferably such that about 80% by weight of the particles have a particle size of more than 75 microns (more than 80% by weight of the particles on Tyler sieve mesh 200) and less than about 10% by weight of the particles have a particle size of more than 2 cm; preferably 80% by weight of the particles have a particle size of more than about 150 microns (80% by weight on Tyler sieve mesh 100) and less than about 10% by weight of the particles have a particle size of more than about 1 cm; or more preferably 80% by weight of the particles have a particle size of more than about 300 microns (80% by weight on Tyler sieve mesh 48) and less than about 10% by weight of the particles have a particle size of more than about 0.5 cm; or even more preferably the particles have an average particle size of from about 500 microns (on Tyler sieve mesh 32) to about 3000 microns, more preferably from about 710 microns (on Tyler mesh sieve 24) to about 1180 microns (through Tyler mesh sieve 14).

30 B. Delayed-release Foam Suppressing Component

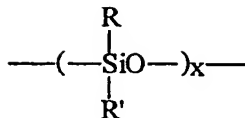
A suds suppressing amount of the delayed-release foam suppressing component is used in the present invention. The term "delayed-release foam suppressing component" means that the foam suppressing component begins to suppress foam over time. Depending on when the foam should be suppressed, the time delay may be adjusted by choosing the appropriate type of foam

suppressing component. The term "suds suppressing amount" is meant that the formulator of the detergent composition selected an amount of this component which will control the suds to the extent desired. The amount of suppressing component will vary with the detergent component selected.

5 A preferred delayed-release foam suppressing component is a silicone foam suppressing component. One preferred silicone foam suppressing component contains a silicone suds controlling agent having an average droplet diameter of from 1 to 50 microns, releasably incorporated in a water-soluble or water dispersible, substantially non-surface active, detergent-impermeable, and
10 non-hygroscopic carrier, the silicone foam suppressing component being substantially free of water-soluble relatively hygroscopic inorganic salts and in the form of an irregularly shaped particle having a minimum dimension of not less than about 0.05 cm and the maximum dimension being at least about 20% greater than the minimum dimension.

15 The preferred suppressing component contains a silicone suds controlling agent which is substantially isolated from the other deterative components of the detergent composition. This "isolation" is achieved by incorporating the controlling agent in a water-soluble or water-dispersible organic carrier matrix. The matrix is preferably a substantially non-surface active, non-hygroscopic
20 material which does not interact with the controlling agent. Moreover, the carrier must be substantially impenetrable by the deterative components to prevent undesirable silicone/detergent and/or silicone/alkalinity interactions. Moreover the carrier matrix herein preferably does not contain added surface active agents, other than the silicone. The carrier is selected such that, upon admixture with
25 water, the carrier matrix dissolves or disperses to release the silicone suds controlling agent to perform its suds or foam controlling function.

 The silicone materials employed as the preferred silicone suds controlling agents herein can be alkylated polysiloxane materials of several types, either singly or in combination with various solid materials such as silica aerogels and
30 xerogels and hydrophobic silicas of various types. In industrial practice, the term "silicone" has become a generic term which encompasses a variety of relatively high molecular weight polymers containing siloxane units and hydrocarbyl groups of various types. In general terms, the silicone suds controllers can be described as siloxanes having the general structure backbone.



wherein x is from 20 to 2,000 and R and R' are each alkyl or aryl groups, especially methyl, ethyl, propyl, butyl or phenyl. The polydimethylsiloxanes (R and R' are methyl) having a molecular weight within the range of from 200 to 200,000, and higher, are all useful as suds controlling agents. Silicone materials are commercially available from the Dow Corning Corporation under the trade name Silicone 200 Fluids®. Suitable polydimethylsiloxanes have a viscosity of from 2×10^{-5} to $1.5 \times 10^{-3} \text{ m}^2\text{s}^{-1}$ (20-1500cs), at 25°C when used with silica and/or siloxane resin.

Additionally, other silicone materials wherein the side chain groups R and R' are alkyl, aryl, or mixed alkyl and aryl hydrocarbonyl groups exhibit useful suds controlling properties. These materials are readily prepared by the hydrolysis of the appropriate alkyl, aryl or mixed alkylaryl or aralkyl silicone dichlorides with water in the manner well known in the art. As specific examples of such silicone suds controlling agents useful herein there can be mentioned, for example, diethyl polysiloxanes; dipropyl polysiloxanes; dibutyl polysiloxanes; methylethyl polysiloxanes; phenylmethyl polysiloxanes; and the like. The dimethyl polysiloxanes are particularly useful herein due to their low cost and ready availability.

The silicone "droplets" in the carrier matrix preferably have an average diameter of about 1 to about 50 μm , preferably from about 5 to about 40 μm , more preferably from about 5 to about 30 μm for maximum effectiveness. Droplets below about 5 μm in diameter are not very effective and above about 30 μm in diameter are increasingly less effective. Similar sizes are required for the other silicone suds controlling agents disclosed hereinafter.

A second highly preferred type of silicone suds controlling agent useful herein comprises a mixture of an alkylated siloxane of the type hereinabove disclosed and solid silica. Such mixtures of silicone and silica can be prepared by affixing the silicone to the surface of silica (SiO_2), for example by means of the catalytic reaction disclosed in U.S. Pat. No. 3,235,509. Suds controlling agents comprising mixtures of silicone and silica prepared in this manner preferably comprise silicone and silica in a silicone:silica ratio of from 19:1 to 1:2, preferably

from 10:1 to 1:1. The silica can be chemically and/or physically bound to the silicone in an amount which is preferably 5% to 20%, preferably from 10 to 15%, by weight, based on the silicone. The particle size of the silica employed in such silica/silicone suds controlling agents should preferably be not more than about 1000, preferably not more than 100 nm, preferably from 5 nm to about 50 nm, more preferably from 10 to 20 nm, and the specific surface area of the silica should exceed about 5 m²/g., preferably more than about 50 m²/g.

Alternatively, suds controlling agents containing silicone and silica can be prepared by admixing a silicone fluid of the type hereinabove disclosed with a hydrophobic silica having a particle size and surface area in the range disclosed above. Any of several known methods may be used for making a hydrophobic silica which can be employed herein in combination with a silicone as the suds controlling agent. For example, a fumed silica can be reacted with a trialkyl chlorosilane (i.e., "silanated") to affix hydrophobic trialkylsilane groups on the surface of the silica. In a preferred and well known process, fumed silica is contacted with trimethylchlorosilane and a preferred hydrophobic silanated silica useful in the present compositions is prepared.

In an alternate procedure, a hydrophobic silica useful in the present compositions is obtained by contacting silica with any of the following compounds: metal, ammonium and substituted ammonium salts of long chain fatty acids, such as sodium stearate, aluminum stearate, and the like; silylhalides, such as ethyltrichlorosilane, butyltrichlorosilane, tricyclohexylchlorosilane, and the like; and long chain alkyl amines or ammonium salts, such as cetyl trimethyl amine, cetyl trimethyl ammonium chloride, and the like.

A preferred suds controlling agent herein comprises a hydrophobic silanated (most preferably trimethylsilanated) silica having a particle size in the range from about 10 nm to about 20 nm and a specific surface area above about 50 m²/g intimately admixed with a dimethyl silicone fluid having a molecular weight in the range of from 500 to 200,000, at a weight ratio of silicone to silanated silica of from 10:1 to 1:2. Such suds controlling agents preferably comprise silicone and the silanated silica in a weight ratio of silicone:silanated silica of from 10:1 to 1:1. The mixed hydrophobic silanated (especially trimethylsilanated) silica-silicone suds controlling agents provide suds control

over a broad range of temperatures, presumably due to the controlled release of the silicone from the surface of the silanated silica.

Another type of suds control agent herein comprises a silicone material of the type hereinabove disclosed sorbed onto and into a solid. Such suds
5 controlling agents comprise the silicone and solid in a silicone:solid ratio of from 20:1 to 1:20, preferably from 5:1 to 1:1. Examples of suitable solid sorbents for the silicones herein include clay, starch, kieselguhr, Fuller's Earth, and the like. The alkalinity of the solid sorbents is of no consequence to the compositions herein, inasmuch as it has been discovered that the silicones are stable
10 when admixed therewith. As disclosed hereinabove, the sorbent-plus-silicone suds controlling agent must be coated or otherwise incorporated into a carrier material of the type hereinafter disclosed to effectively isolate the silicone from the detergent component of the instant compositions.

Yet another preferred type of silicone suds controlling agent herein
15 comprises a silicone fluid, a silicone resin and silica. The silicone fluids useful in such suds controlling mixtures are any of the types hereinabove disclosed, but are preferably dimethyl silicones. The silicone "resins" used in such compositions can be any alkylated silicone resins, but are usually those prepared from methylsilanes. Silicone resins are commonly described as "three-dimensional"
20 polymers arising from the hydrolysis of alkyl trichlorosilanes, whereas the silicone fluids are "two-dimensional" polymers prepared by the hydrolysis of dichlorosilanes. The silica components of such compositions are microporous materials such as the fumed silica aerogels and xerogels having the particle sizes and surface areas hereinabove disclosed.

25 The mixed silicone fluid/silicone resin/silica materials useful in the present compositions can be prepared in the manner disclosed in U.S. Pat. No. 3,455,839. These mixed materials are commercially available from the Dow Corning Corporation. According to U.S. Pat. No. 3,455,839, such materials can be described as mixtures consisting essentially of: for each 100 parts by weight
30 of a polydimethylsiloxane fluid having a viscosity in the range from 2×10^{-5} to $1.5 \times 10^{-3} \text{ m}^2\text{s}^{-1}$ (20cs. to 1500cs.) at 25°C, (a) from 5 to 50, preferably from 5 to 20, parts by weight of a siloxane resin composed of $(\text{CH}_3)_3\text{SiO}_{1/2}$ units and SiO_2 units in which the ratio of the $(\text{CH}_3)_3\text{SiO}_{1/2}$ units to the SiO_2 units is within the range of from about 0.6/1 to about 1.2/1; and (b) from 1 to 10, preferably from 1 to 5, parts
35 by weight of a solid silica gel, preferably an aerogel.

Again, such mixed silicone/silicone resin/silica suds controlling agents must be combined with a detergent-impermeable carrier material to be useful in the compositions herein.

5 The silicone suds controlling agents of the aforementioned type is preferably incorporated within (i.e., coated, encapsulated, covered by, internalized, or otherwise substantially contained within) a substantially water-soluble, or water-dispersible, and non-hydrosopic carrier material which must be impermeable to detergents and alkalinity and which, itself, must be substantially nonsurface active. By substantially nonsurface active is meant that the carrier
10 material, itself, does not interact with the silicone material in such fashion that the silicone material is emulsified or otherwise excessively dispersed prior to its release in the wash water. I.e., the particle size of the silicone droplet should be maintained above 1, more preferably above 5 mm.

Of course, when preparing a dry powder or granulated detergent
15 composition, it is preferable that the silicone suds controlling component thereof also be substantially dry and nontacky at ambient temperatures. Accordingly, it is preferred herein to use as the carrier material, or vehicle, plastic, organic compounds which can be conveniently melted, admixed with the silicone suds controlling agent, and thereafter cooled to form solid flakes. There are a wide
20 variety of such carrier materials useful herein. Since the silicone suds controlling agent is to be releasably incorporated in the carrier, such that the silicone is released into the aqueous bath upon admixture of the composition therewith, it is preferred that the carrier material be water soluble. However, water-dispersible materials are also useful, inasmuch as they will also release the silicone upon
25 addition to an aqueous bath.

A wide variety of carrier materials having the requisite solubility/dispersibility characteristics and the essential features of being substantially non-surface active, substantially non-hydrosopic and substantially detergent-impermeable are known. However, polyethylene glycol (PEG) which
30 has substantially no surface active characteristics is highly preferred herein. PEG, having molecular weights of from 1,500 to 100,000, preferably from 3,000 to 20,000, more preferably from 5,000 to 10,000 can be used.

Surprisingly, highly ethoxylated fatty alcohols such as tallow alcohol condensed with at least about 25 molar proportions of ethylene oxide are also
35 useful herein. Other alcohol condensates containing extremely high ethoxylate

proportions (25 and above) are also useful herein. Such high ethoxylates apparently lack sufficient surface active characteristics to interact or otherwise interfere with the desired suds control properties of the silicone agents herein. A variety of other materials useful as the carrier agents herein can also be used,
5 e.g., gelatin; agar; gum arabic; and various algae-derived gels.

A very preferred carrier material is a mixture of from 0.2% to 15%, preferably from 0.25% to 5%, more preferably from 0.25% to 2% of fatty acids containing from 12 to 30, preferably from 14 to 20, more preferably from 14 to 16, carbon atoms and the balance PEG. Such a carrier material gives a more
10 desirable suds pattern over the duration of the washing process, providing more suds at the start and less suds at the end than PEG alone. The fatty acid delays the solubility of the suds suppressor particle and thereby delays the release of the silicone. Soap and/or wax may also be used in place of the fatty acid.

The preferred irregularly shaped particulate silicone suds controlling
15 component can be conveniently prepared in a highly preferred flake form by admixing the silicone suds controlling agent with a molten carrier material, mixing to form the appropriate silicone droplet size, and flaking, e.g., by milling or extruding to form a thin sheet, cooling to solidify the carrier material, and breaking the sheet into particles of the right size. In another preferred process
20 thin films can be formed by cooling molten carrier material with the suds suppressor dispersed therein on, e.g., a chill roll or belt cooler and then breaking said film into appropriate sized flakes. The thickness of the flake should be from 0.05 to 0.15 cm, preferably from 0.05 to 0.1 cm. When this procedure is used, the silicone suds controlling agent is contained within the carrier material so
25 effectively that when this material is eventually admixed with, or incorporated into, a detergent composition, the silicone does not substantially come into contact with the detergent surfactant ingredient.

In order to provide a granular, nontacky suds controlling component useful in dry granular detergent compositions, the flake of the silicone suds controlling
30 agent and carrier material should be substantially solidified. This can be achieved by use of belt coolers and which quickly cool the sheets or flakes such that the carrier melt is hardened. Extrusion techniques can also be used.

It is to be recognized that the amount of carrier used to isolate the silicone suds controlling agent herein from the detergent component of the compositions
35 herein is not critical. It is only necessary that enough carrier be used to provide

sufficient volume that substantially all the silicone can be incorporated therein. Likewise, it is preferred to have sufficient carrier material to provide for sufficient strength of the resultant granule to resist premature breakage. Generally, above a 2:1, preferably from 5:1 to 100:1, more preferably from 20:1 to 40:1, weight ratio of carrier to silicone suds controlling agent is employed.

The size of the particles of the suds controlling component used in the present compositions is selected to be compatible with the remainder of the detergent composition. The suds controlling components herein do not segregate unacceptably within the detergent composition. In general, particles with a maximum dimension of from 600 to 2000, preferably from 800 to 1600 μm are compatible with spray-dried detergent granules. Therefore, the majority of the particles should have these maximum dimensions. The majority of the particles should have a ratio of the maximum to the minimum diameter of from 1.5:1 to 5:1, preferably from 1.5:1 to 4:1.

Other alternative suds controlling components which can be releasably incorporated in a carrier material besides silicone, include monocarboxylic fatty acids and soluble salts thereof. These typically have hydrocarbyl chains of 10 to 24 carbon atoms, preferably 12 to 18 carbon atoms. Suitable salts include the alkali metal salts such as sodium, potassium, and lithium salts, and ammonium and alkanolammonium salts. Other suitable suds controlling components include high molecular weight fatty esters (e.g. fatty acid triglycerides), fatty acid esters of monovalent alcohols, aliphatic C18-C40 ketones (e.g. stearone) N-alkylated amino triazines such as tri- to hexa-alkylmelamines or di- to tetra alkyl diamine chlortriazines formed as products of cyanuric chloride with two or three moles of a primary or secondary amine containing 1 to 24 carbon atoms, propylene oxide, bis stearic acid amide and monostearyl di-alkali metal (e.g. sodium, potassium, lithium) phosphates and phosphate esters.

In addition to the above-mentioned silicone foam suppressing component, other delayed-release foam suppressing components may be used. For example, an encapsulated antifoam composition having a suds controlling agent and the reaction product of (i) an alkylalkoxysilane; and (ii) a silicone condensation cure catalyst wherein the suds controlling agent is encapsulated by the reaction product may be used. The method of making such preferred encapsulated antifoam compositions are described in GB 2 318 355, published on April 22, 1998, by General Electric Co. In another example, a homogenous

rosin/silicone mixture made from a mixture of liquid polydimethyl siloxane with aqueous caustic soda solution and melted rosin can also be used as a delayed-release foam suppressing component. Because the rosin/silicone mixture becomes soluble at higher temperatures, such foam suppressing is especially
5 useful for the delayed-release in washing conditions in which the wash water is heated over time. See also GB 1340043, published December 5, 1978, by Griffiths et. al.

In another example for a silicone based foam suppressing component, the carrier for the suds controlling agent can be a solid particulate structure of
10 modified cellulose which is soluble in water, but dissolves at a relatively slow rate due to the swelling of the surface of the cellulose. For examples of a preferred process for making such foam suppressing components, please see US 4,894,177, Starch et al., granted January 16, 1990 to Dow Corning Corp. In yet another example, a suds controlling agent can be enclosed in a microcapsule
15 composed of a core and a shell of a polymer, so that there is a controlled release of the core material (suds controlling agent) by destruction of the polymer shell by the action of bases.

In another example, microcapsules can be used as a delayed-release foam suppressing component. One preferred microcapsule is made by
20 polymerizing (i) more than 40% by weight of maleic anhydride, (ii) 0-99% by weight of at least one monoethylenically unsaturated monomer which is oil-soluble and which is different from the monomers of maleic anhydride, (iii) 0-80% by weight of crosslinking monomers which are oil soluble and different from maleic anhydride which have at least two monoethylenically
25 unsaturated non-conjugated double bonds in the molecule, and (iv) 0-20% by weight of water-soluble monoethylenically unsaturated monomers, the percentages relating to the total amount of monomers (i) to (iv), in the oil phase of a stable oil-in-water emulsion in the presence of polymerization initiators which form free radicals, where the temperature of the polymerizing reaction mixture
30 may be continuously or periodically increased during the polymerization. For a detailed process description, see US 5,596,051, Jahns et. al., granted on January 21, 1997 to BASF.

C. Detersive components

The detergent composition of the invention can comprise additional
35 detersive components known in the art. In addition, the foaming component

and/or the delayed-release foam suppressing component may further contain
deterative components. The precise nature of these additional components, and
levels of incorporation thereof will depend on the physical form of the
composition, and the precise nature of the washing operation for which it is to be
used.

The detergent compositions preferably contains one or more additional
deterative components selected from the group consisting of surfactants,
bleaches, alkali metal salt of silicate, builders, chelating agents, enzymes, fillers,
soil suspending agents, optical brighteners, dispersants, soil release agents,
photoactivated bleaches, dyes, dye transfer inhibitors, pigments, perfumes, clay
softening system, cationic fabric softening agents, and mixtures thereof.

In particular, it can be preferred that the particles comprises at least one or
more anionic surfactants and preferably one or more cationic surfactants, as
described herein. It can also be preferred that the particles also, or alternatively
comprise builder material and bleaching species, as described herein

The detergent compositions may contain one or more surfactants
selected from anionic, cationic, ampholytic, amphoteric and zwitterionic
surfactants or nonionic surfactants as described above, and mixtures thereof. A
typical listing of these surfactants, is given in U.S.P. 3,929,678 issued to Laughlin
and Heuring on December 30, 1975. Further examples are given in "Surface
Active Agents and Detergents" (Vol. I and II by Schwartz, Perry and Berch). A list
of suitable cationic surfactants is given in U.S.P. 4,259,217 issued to Murphy on
March 31, 1981.

Anionic Surfactant

Any anionic surfactant useful for deterative purposes is suitable. Examples
include salts (including, for example, sodium, potassium, ammonium, and
substituted ammonium salts such as mono-, di- and triethanolamine salts) of the
anionic sulfate, sulfonate, carboxylate and sarcosinate surfactants. Anionic
sulfate surfactants are preferred.

Other anionic surfactants include the isethionates such as the acyl
isethionates, N-acyl taurates, fatty acid amides of methyl tauride, alkyl succinates
and sulfosuccinates, monoesters of sulfosuccinate (especially saturated and
unsaturated C₁₂-C₁₈ monoesters) diesters of sulfosuccinate (especially
saturated and unsaturated C₆-C₁₄ diesters), N-acyl sarcosinates. Resin acids
and hydrogenated resin acids are also suitable, such as rosin, hydrogenated

rosin, and resin acids and hydrogenated resin acids present in or derived from tallow oil.

The anionic surfactant can be present at a level of 0.5% to 80%, preferably at a level of from 3% to 60%, more preferably of from 5% to 35% by weight of the composition or the particle. The ratio of the stabilising agent to the anionic surfactant is preferably from 1:20 to 20:1, more preferably from 1:6 to 6:1.

Anionic Sulfate Surfactant

Anionic sulfate surfactants suitable for use herein include the linear and branched primary and secondary alkyl sulfates, alkyl ethoxysulfates, fatty oleoyl glycerol sulfates, alkyl phenol ethylene oxide ether sulfates, the C₅-C₁₇ acyl-N-(C₁-C₄ alkyl) and -N-(C₁-C₂ hydroxyalkyl) glucamine sulfates, and sulfates of alkylpolysaccharides such as the sulfates of alkylpolyglucoside (the nonionic nonsulfated compounds being described herein).

Alkyl sulfate surfactants are preferably selected from the linear and branched primary C₉-C₂₂ alkyl sulfates, more preferably the C₁₁-C₁₅ branched chain alkyl sulfates and the C₁₂-C₁₄ linear chain alkyl sulfates.

Alkyl ethoxysulfate surfactants are preferably selected from the group consisting of the C₁₀-C₁₈ alkyl sulfates which have been ethoxylated with from 0.5 to 50 moles of ethylene oxide per molecule. More preferably, the alkyl ethoxysulfate surfactant is a C₁₁-C₁₈, most preferably C₁₁-C₁₅ alkyl sulfate which has been ethoxylated with from 0.5 to 7, preferably from 1 to 5, moles of ethylene oxide per molecule.

A particularly preferred aspect of the invention employs mixtures of the preferred alkyl sulfate and alkyl ethoxysulfate surfactants. Such mixtures have been disclosed in PCT Patent Application No. WO 93/18124.

Anionic Sulfonate Surfactant

Anionic sulfonate surfactants suitable for use herein include the salts of C₅-C₂₀ linear or branched alkylbenzene sulfonates, alkyl ester sulfonates, in particular methyl ester sulfonates, C₆-C₂₂ primary or secondary alkane sulfonates, C₆-C₂₄ olefin sulfonates, sulfonated polycarboxylic acids, alkyl glycerol sulfonates, fatty acyl glycerol sulfonates, fatty oleyl glycerol sulfonates, and any mixtures thereof

Anionic Carboxylate Surfactant

Suitable anionic carboxylate surfactants include the alkyl ethoxy carboxylates, the alkyl polyethoxy polycarboxylate surfactants and the soaps ('alkyl carboxyls'), especially certain secondary soaps as described herein.

Suitable alkyl ethoxy carboxylates include those with the formula
5 $RO(CH_2CH_2O)_xCH_2COO-M^+$ wherein R is a C₆ to C₁₈ alkyl group, x ranges from 0 to 10, and the ethoxylate distribution is such that, on a weight basis, the amount of material where x is 0 is less than 20 % and M is a cation. Suitable alkyl polyethoxy polycarboxylate surfactants include those having the formula
10 $RO-(CHR_1-CHR_2-O)_x-R_3$ wherein R is a C₆ to C₁₈ alkyl group, x is from 1 to 25, R₁ and R₂ are selected from the group consisting of hydrogen, methyl acid radical, succinic acid radical, hydroxysuccinic acid radical, and mixtures thereof, and R₃ is selected from the group consisting of hydrogen, substituted or unsubstituted hydrocarbon having between 1 and 8 carbon atoms, and mixtures thereof.

15 Suitable soap surfactants include the secondary soap surfactants which contain a carboxyl unit connected to a secondary carbon. Preferred secondary soap surfactants for use herein are water-soluble members selected from the group consisting of the water-soluble salts of 2-methyl-1-undecanoic acid, 2-ethyl-1-decanoic acid, 2-propyl-1-nonanoic acid, 2-butyl-1-octanoic acid and 2-
20 pentyl-1-heptanoic acid. Certain soaps may also be included as suds suppressors.

Alkali Metal Sarcosinate Surfactant

Other suitable anionic surfactants are the alkali metal sarcosinates of formula R-CON(R¹)CH₂COOM, wherein R is a C₅-C₁₇ linear or branched alkyl
25 or alkenyl group, R¹ is a C₁-C₄ alkyl group and M is an alkali metal ion. Preferred examples are the myristyl and oleoyl methyl sarcosinates in the form of their sodium salts.

Cationic Surfactant

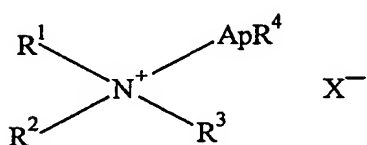
Another preferred surfactant is a cationic surfactant, which may preferably
30 be present at a level of from 0.1% to 60% by weight of the composition or particle, more preferably from 0.4% to 20%, most preferably from 0.5% to 5% by weight of the composition. When present, the ratio of the anionic surfactant to the cationic surfactant is preferably from 25:1 to 1:3, more preferably from 15:1 to 1:1. most preferably from 10:1 to 1:1 The ratio of cationic surfactant to the

stabilising agent is preferably from 1:30 to 20:1, more preferably from 1:20 to 10:1.

Preferably the cationic surfactant is selected from the group consisting of cationic ester surfactants, cationic mono-alkoxylated amine surfactants, cationic bis-alkoxylated amine surfactants and mixtures thereof.

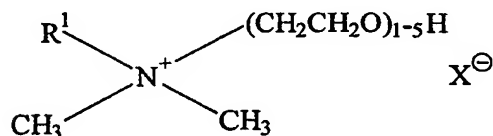
Cationic Mono-Alkoxylated Amine Surfactants

The optional cationic mono-alkoxylated amine surfactant for use herein, has the general formula:



wherein R^1 is an alkyl or alkenyl moiety containing from about 6 to about 18 carbon atoms, preferably 6 to about 16 carbon atoms, most preferably from about 6 to about 11 carbon atoms; R^2 and R^3 are each independently alkyl groups containing from one to about three carbon atoms, preferably methyl; R^4 is selected from hydrogen (preferred), methyl and ethyl, X^- is an anion such as chloride, bromide, methylsulfate, sulfate, or the like, to provide electrical neutrality; A is selected from C_1 - C_4 alkoxy, especially ethoxy (i.e., $-\text{CH}_2\text{CH}_2\text{O}-$), propoxy, butoxy and mixtures thereof; and p is from 1 to about 30, preferably 1 to about 15, most preferably 1 to about 8.

Highly preferred cationic mono-alkoxylated amine surfactants for use herein are of the formula



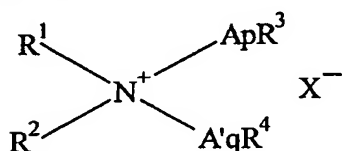
wherein R^1 is C_6 - C_{18} hydrocarbyl and mixtures thereof, preferably C_6 - C_{14} , especially C_6 - C_{11} alkyl, preferably C_8 and C_{10} alkyl, and X is any convenient anion to provide charge balance, preferably chloride or bromide.

As noted, compounds of the foregoing type include those wherein the ethoxy ($\text{CH}_2\text{CH}_2\text{O}$) units (EO) are replaced by butoxy, isopropoxy

[CH(CH₃)CH₂O] and [CH₂CH(CH₃O)] units (i-Pr) or n-propoxy units (Pr), or mixtures of EO and/or Pr and/or i-Pr units.

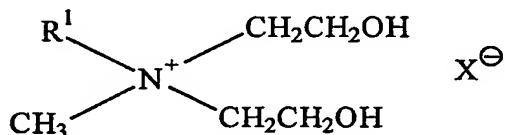
Cationic Bis-Alkoxyated Amine Surfactant

The cationic bis-alkoxyated amine surfactant for use herein, has the general formula:



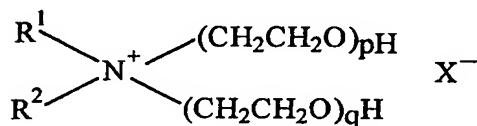
wherein R¹ is an alkyl or alkenyl moiety containing from about 6 to about 18 carbon atoms, preferably 6 to about 16 carbon atoms, more preferably 6 to about 11, most preferably from about 8 to about 10 carbon atoms; R² is an alkyl group containing from one to three carbon atoms, preferably methyl; R³ and R⁴ can vary independently and are selected from hydrogen (preferred), methyl and ethyl, X⁻ is an anion such as chloride, bromide, methylsulfate, sulfate, or the like, sufficient to provide electrical neutrality. A and A' can vary independently and are each selected from C₁-C₄ alkoxy, especially ethoxy, (i.e., -CH₂CH₂O-), propoxy, butoxy and mixtures thereof; p is from 1 to about 30, preferably 1 to about 4 and q is from 1 to about 30, preferably 1 to about 4, and most preferably both p and q are 1.

Highly preferred cationic bis-alkoxyated amine surfactants for use herein are of the formula



wherein R¹ is C₆-C₁₈ hydrocarbyl and mixtures thereof, preferably C₆, C₈, C₁₀, C₁₂, C₁₄ alkyl and mixtures thereof. X is any convenient anion to provide charge balance, preferably chloride. With reference to the general cationic bis-alkoxyated amine structure noted above, since in a preferred compound R¹ is derived from (coconut) C₁₂-C₁₄ alkyl fraction fatty acids, R² is methyl and ApR³ and A'qR⁴ are each monoethoxy.

Other cationic bis-alkoxylated amine surfactants useful herein include compounds of the formula:



wherein R^1 is C_6 - C_{18} hydrocarbyl, preferably C_6 - C_{14} alkyl, independently p is 1 to about 3 and q is 1 to about 3, R^2 is C_1 - C_3 alkyl, preferably methyl, and X is an anion, especially chloride or bromide.

Other compounds of the foregoing type include those wherein the ethoxy $(\text{CH}_2\text{CH}_2\text{O})$ units (EO) are replaced by butoxy (Bu) isopropoxy $[\text{CH}(\text{CH}_3)\text{CH}_2\text{O}]$ and $[\text{CH}_2\text{CH}(\text{CH}_3)\text{O}]$ units (i-Pr) or n-propoxy units (Pr), or mixtures of EO and/or Pr and/or i-Pr units.

Amphoteric Surfactant

Suitable amphoteric surfactants for use herein include the amine oxide surfactants and the alkyl amphocarboxylic acids. Suitable amine oxides include those compounds having the formula $\text{R}^3(\text{OR}^4)_x\text{N}^0(\text{R}^5)_2$ wherein R^3 is selected from an alkyl, hydroxyalkyl, acylamidopropoyl and alkyl phenyl group, or mixtures thereof, containing from 8 to 26 carbon atoms; R^4 is an alkylene or hydroxyalkylene group containing from 2 to 3 carbon atoms, or mixtures thereof; x is from 0 to 5, preferably from 0 to 3; and each R^5 is an alkyl or hydroxyalkyl group containing from 1 to 3, or a polyethylene oxide group containing from 1 to 3 ethylene oxide groups. Preferred are C_{10} - C_{18} alkyl dimethylamine oxide, and C_{10} - C_{18} acylamido alkyl dimethylamine oxide. A suitable example of an alkyl amphocarboxylic acid is Miranol(TM) C2M Conc. manufactured by Miranol, Inc., Dayton, NJ.

Zwitterionic Surfactant

Zwitterionic surfactants can also be incorporated into the particle of the invention or the compositions containing the particle of the invention. These surfactants can be broadly described as derivatives of secondary and tertiary amines, derivatives of heterocyclic secondary and tertiary amines, or derivatives of quaternary ammonium, quaternary phosphonium or tertiary sulfonium compounds. Betaine and sultaine surfactants are exemplary zwitterionic

surfactants for use herein. Suitable betaines are those compounds having the formula $R(R^1)_2N^+R^2COO^-$ wherein R is a C₆-C₁₈ hydrocarbyl group, each R¹ is typically C₁-C₃ alkyl, and R² is a C₁-C₅ hydrocarbyl group. Preferred betaines are C₁₂-18 dimethyl-ammonio hexanoate and the C₁₀-18 acylamidopropane (or ethane) dimethyl (or diethyl) betaines. Complex betaine surfactants are also suitable for use herein.

Water-Soluble Builder Compound

The compositions preferably contain a water-soluble builder compound, typically present at a level of from 1% to 80% by weight, preferably from 10% to 70% by weight, most preferably from 20% to 60% by weight of the composition or particle.

Suitable water-soluble builder compounds include the water soluble monomeric polycarboxylates, or their acid forms, homo or copolymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxylic radicals separated from each other by not more than two carbon atoms, borates, phosphates, and mixtures of any of the foregoing.

The carboxylate or polycarboxylate builder can be monomeric or oligomeric in type although monomeric polycarboxylates are generally preferred for reasons of cost and performance.

Suitable carboxylates containing one carboxy group include the water soluble salts of lactic acid, glycolic acid and ether derivatives thereof. Polycarboxylates containing two carboxy groups include the water-soluble salts of succinic acid, malonic acid, (ethylenedioxy) diacetic acid, maleic acid, diglycolic acid, tartaric acid, tartronic acid and fumaric acid, as well as the ether carboxylates and the sulfinyl carboxylates. Polycarboxylates containing three carboxy groups include, in particular, water-soluble citrates, aconitrates and citraconates as well as succinate derivatives such as the carboxymethyloxysuccinates described in British Patent No. 1,379,241, lactoxysuccinates described in British Patent No. 1,389,732, and aminosuccinates described in Netherlands Application 7205873, and the oxypolycarboxylate materials such as 2-oxa-1,1,3-propane tricarboxylates described in British Patent No. 1,387,447.

Polycarboxylates containing four carboxy groups include oxydisuccinates disclosed in British Patent No. 1,261,829, 1,1,2,2-ethane tetracarboxylates, 1,1,3,3-propane tetracarboxylates and 1,1,2,3-propane tetracarboxylates.

Polycarboxylates containing sulfo substituents include the sulfosuccinate derivatives disclosed in British Patent Nos. 1,398,421 and 1,398,422 and in U.S. Patent No. 3,936,448, and the sulfonated pyrolysed citrates described in British Patent No. 1,439,000. Preferred polycarboxylates are hydroxycarboxylates containing up to three carboxy groups per molecule, more particularly citrates.

Borate builders, as well as builders containing borate-forming materials that can produce borate under detergent storage or wash conditions are useful water-soluble builders herein.

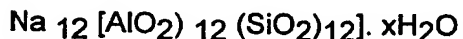
Suitable examples of water-soluble phosphate builders are the alkali metal tripolyphosphates, sodium, potassium and ammonium pyrophosphate, sodium and potassium and ammonium pyrophosphate, sodium and potassium orthophosphate, sodium polymeta/phosphate in which the degree of polymerization ranges from about 6 to 21, and salts of phytic acid.

Partially Soluble or Insoluble Builder Compound

The composition may contain a partially soluble or insoluble builder compound, typically present at a level of from 1% to 80% by weight, preferably from 10% to 70% by weight, most preferably from 20% to 60% weight of the composition or particle.

Examples of largely water insoluble builders include the sodium aluminosilicates. Suitable aluminosilicate zeolites have the unit cell formula $\text{Na}_z[(\text{AlO}_2)_z(\text{SiO}_2)_y] \cdot x\text{H}_2\text{O}$ wherein z and y are at least 6; the molar ratio of z to y is from 1.0 to 0.5 and x is at least 5, preferably from 7.5 to 276, more preferably from 10 to 264. The aluminosilicate material are in hydrated form and are preferably crystalline, containing from 10% to 28%, more preferably from 18% to 22% water in bound form.

The aluminosilicate zeolites can be naturally occurring materials, but are preferably synthetically derived. Synthetic crystalline aluminosilicate ion exchange materials are available under the designations Zeolite A, Zeolite B, Zeolite P, Zeolite X, Zeolite HS and mixtures thereof. Zeolite A has the formula



wherein x is from 20 to 30, especially 27. Zeolite X has the formula $\text{Na}_{86} [(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}] \cdot 276 \text{H}_2\text{O}$.

Preferred crystalline layered silicates for use herein have the general formula



5 wherein M is sodium or hydrogen, x is a number from 1.9 to 4 and y is a number from 0 to 20. Crystalline layered sodium silicates of this type are disclosed in EP-A-0164514 and methods for their preparation are disclosed in DE-A-3417649 and DE-A-3742043. Herein, x in the general formula above preferably has a
10 value of 2, 3 or 4 and is preferably 2. The most preferred material is $\delta\text{-Na}_2\text{Si}_2\text{O}_5$, available from Hoechst AG as NaSKS-6.

Perhydrate Bleaches

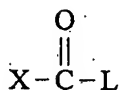
15 An preferred additional components of the composition is a perhydrate bleach, such as metal perborates, metal percarbonates, particularly the sodium salts. Perborate can be mono or tetra hydrated. Sodium percarbonate has the formula corresponding to $2\text{Na}_2\text{CO}_3\cdot 3\text{H}_2\text{O}_2$, and is available commercially as a crystalline solid. Potassium peroxymonopersulfate, sodium per is another optional inorganic perhydrate salt of use in the detergent compositions herein.

Organic Peroxyacid Bleaching System

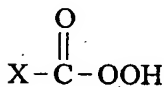
20 A preferred feature of compositions is an organic peroxyacid bleaching system. In one preferred execution the bleaching system contains a hydrogen peroxide source and an organic peroxyacid bleach precursor compound. The production of the organic peroxyacid occurs by an in situ reaction of the precursor with a source of hydrogen peroxide. Preferred sources of hydrogen
25 peroxide include inorganic perhydrate bleaches, such as the perborate bleach of the claimed invention. In an alternative preferred execution a preformed organic peroxyacid is incorporated directly into the composition. Compositions containing mixtures of a hydrogen peroxide source and organic peroxyacid precursor in combination with a preformed organic peroxyacid are also envisaged.

Peroxyacid Bleach Precursor

30 Peroxyacid bleach precursors are compounds which react with hydrogen peroxide in a perhydrolysis reaction to produce a peroxyacid. Generally peroxyacid bleach precursors may be represented as



where L is a leaving group and X is essentially any functionality, such that on perhydrolysis the structure of the peroxyacid produced is



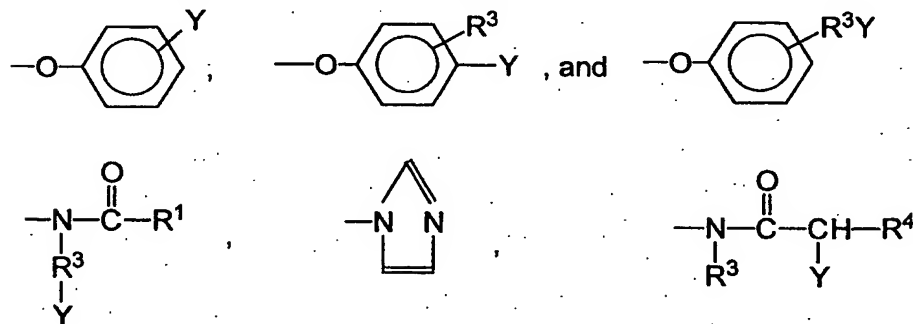
Peroxyacid bleach precursor compounds are preferably incorporated at a level of from 0.5% to 80% by weight of the particle, more preferably from 5% to 45% by weight, most preferably from 3% to 15% by weight of the compositions.

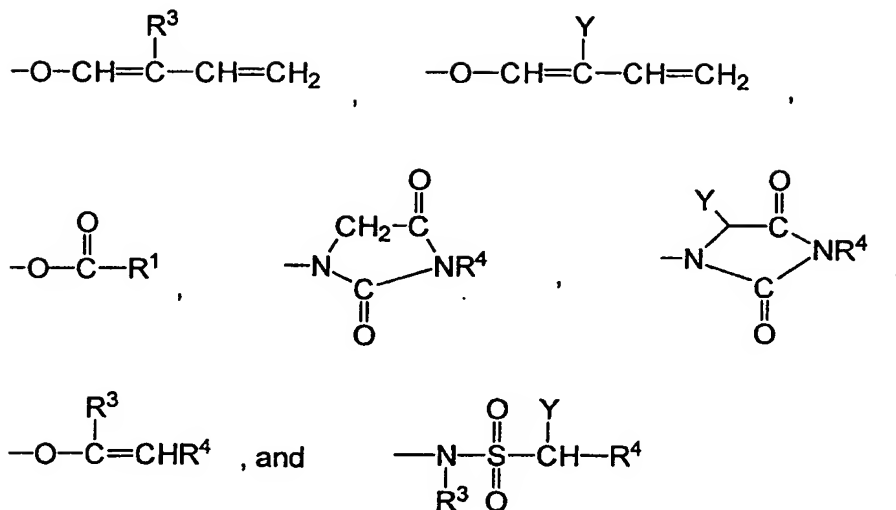
Suitable peroxyacid bleach precursor compounds typically contain one or more N- or O-acyl groups, which precursors can be selected from a wide range of classes. Suitable classes include anhydrides, esters, imides, lactams and acylated derivatives of imidazoles and oximes. Examples of useful materials within these classes are disclosed in GB-A-1586789. Suitable esters are disclosed in GB-A-836988, 864798, 1147871, 2143231 and EP-A-0170386.

Leaving Groups

The leaving group, hereinafter L group, must be sufficiently reactive for the perhydrolysis reaction to occur within the optimum time frame (e.g., a wash cycle). However, if L is too reactive, this activator will be difficult to stabilize for use in a bleaching composition.

Preferred L groups are selected from the group consisting of:





5

and mixtures thereof, wherein R^1 is an alkyl, aryl, or alkaryl group containing from 1 to 14 carbon atoms, R^3 is an alkyl chain containing from 1 to 8 carbon atoms, R^4 is H or R^3 , and Y is H or a solubilizing group. Any of R^1 , R^3 and R^4 may be substituted by essentially any functional group including, for example

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alkyl, hydroxy, alkoxy, halogen, amine, nitrosyl, amide and ammonium or alkyl ammonium groups.

The preferred solubilizing groups are $-\text{SO}_3^-\text{M}^+$, $-\text{CO}_2^-\text{M}^+$, $-\text{SO}_4^-\text{M}^+$, $-\text{N}^+(\text{R}^3)_4\text{X}^-$ and $\text{O}-\text{N}(\text{R}^3)_3$ and most preferably $-\text{SO}_3^-\text{M}^+$ and $-\text{CO}_2^-\text{M}^+$ wherein R^3 is an alkyl chain containing from 1 to 4 carbon atoms, M is a cation which provides solubility to the bleach activator and X is an anion which provides solubility to the bleach activator. Preferably, M is an alkali metal, ammonium or substituted ammonium cation, with sodium and potassium being most preferred, and X is a halide, hydroxide, methylsulfate or acetate anion.

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Alkyl Percarboxylic Acid Bleach Precursors

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Alkyl percarboxylic acid bleach precursors form percarboxylic acids on perhydrolysis. Preferred precursors of this type provide peracetic acid on perhydrolysis. Preferred alkyl percarboxylic precursor compounds of the imide type include the N-,N,N¹N¹ tetra acetylated alkylene diamines wherein the alkylene group contains from 1 to 6 carbon atoms, particularly those compounds

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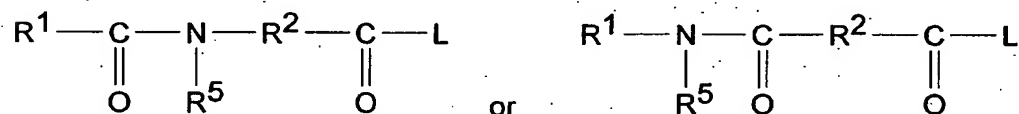
in which the alkylene group contains 1, 2 and 6 carbon atoms. Tetraacetyl ethylene diamine (TAED) is particularly preferred. The TAED is preferably not

present in the agglomerated particle of the present invention, but preferably present in the detergent composition, comprising the particle.

Other preferred alkyl percarboxylic acid precursors include sodium 3,5,5-tri-methyl hexanoyloxybenzene sulfonate (iso-NOBS), sodium nonanoyloxybenzene sulfonate (NOBS), sodium acetoxylbenzene sulfonate (ABS) and pentaacetyl glucose.

Amide Substituted Alkyl Peroxyacid Precursors

Amide substituted alkyl peroxyacid precursor compounds are suitable herein, including those of the following general formulae:



wherein R^1 is an alkyl group with from 1 to 14 carbon atoms, R^2 is an alkylene group containing from 1 to 14 carbon atoms, and R^5 is H or an alkyl group containing 1 to 10 carbon atoms and L can be essentially any leaving group.

Amide substituted bleach activator compounds of this type are described in EP-A-0170386.

Perbenzoic Acid Precursor

Perbenzoic acid precursor compounds provide perbenzoic acid on perhydrolysis. Suitable O-acylated perbenzoic acid precursor compounds include the substituted and unsubstituted benzoyl oxybenzene sulfonates, and the benzoylation products of sorbitol, glucose, and all saccharides with benzoylating agents, and those of the imide type including N-benzoyl succinimide, tetrabenzoyl ethylene diamine and the N-benzoyl substituted ureas. Suitable imidazole type perbenzoic acid precursors include N-benzoyl imidazole and N-benzoyl benzimidazole. Other useful N-acyl group-containing perbenzoic acid precursors include N-benzoyl pyrrolidone, dibenzoyl taurine and benzoyl pyroglutamic acid.

Cationic Peroxyacid Precursors

Cationic peroxyacid precursor compounds produce cationic peroxyacids on perhydrolysis. Typically, cationic peroxyacid precursors are formed by substituting the peroxyacid part of a suitable peroxyacid precursor compound with a positively charged functional group, such as an ammonium or alkyl

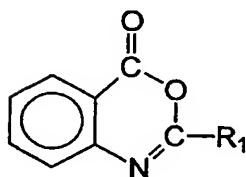
ammonium group, preferably an ethyl or methyl ammonium group. Cationic peroxyacid precursors are typically present in the solid detergent compositions as a salt with a suitable anion, such as a halide ion.

The peroxyacid precursor compound to be so cationically substituted may be a perbenzoic acid, or substituted derivative thereof, precursor compound as described hereinbefore. Alternatively, the peroxyacid precursor compound may be an alkyl percarboxylic acid precursor compound or an amide substituted alkyl peroxyacid precursor as described hereinafter. Cationic peroxyacid precursors are described in U.S. Patents 4,904,406; 4,751,015; 4,988,451; 4,397,757; 5,269,962; 5,127,852; 5,093,022; 5,106,528; U.K. 1,382,594; EP 475,512, 458,396 and 284,292; and in JP 87-318,332. Examples of preferred cationic peroxyacid precursors are described in UK Patent Application No. 9407944.9 and US Patent Application Nos. 08/298903, 08/298650, 08/298904 and 08/298906.

Suitable cationic peroxyacid precursors include any of the ammonium or alkyl ammonium substituted alkyl or benzoyl oxybenzene sulfonates, N-acylated caprolactams, and monobenzoyltetraacetyl glucose benzoyl peroxides. Preferred cationic peroxyacid precursors of the N-acylated caprolactam class include the trialkyl ammonium methylene benzoyl caprolactams and the trialkyl ammonium methylene alkyl caprolactams.

Benzoxazin Organic Peroxyacid Precursors

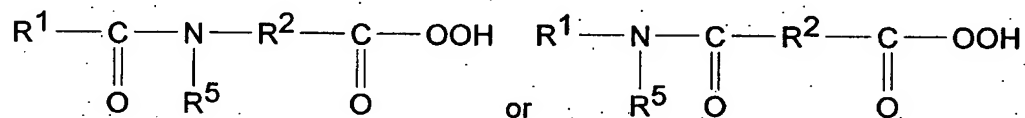
Also suitable are precursor compounds of the benzoxazin-type, as disclosed for example in EP-A-332,294 and EP-A-482,807, particularly those having the formula:



wherein R₁ is H, alkyl, alkaryl, aryl, or arylalkyl.

Preformed Organic Peroxyacid

The organic peroxyacid bleaching system may contain, in addition to, or as an alternative to, an organic peroxyacid bleach precursor compound, a preformed organic peroxyacid, typically at a level of from 1% to 15% by weight, more preferably from 1% to 10% by weight of the composition. A preferred class of organic peroxyacid compounds are the amide substituted compounds of the following general formulae:



wherein R¹ is an alkyl, aryl or alkaryl group with from 1 to 14 carbon atoms, R² is an alkylene, arylene, and alkarylene group containing from 1 to 14 carbon atoms, and R⁵ is H or an alkyl, aryl, or alkaryl group containing 1 to 10 carbon atoms. Amide substituted organic peroxyacid compounds of this type are described in EP-A-0170386. Other organic peroxyacids include diacyl and tetraacylperoxides, especially diperoxydodecanedioic acid, diperoxytetradecanedioic acid and diperoxyhexadecanedioic acid. Mono- and diperazelaic acid, mono- and diperbrassylic acid and N-phthaloylaminoperoxicaproic acid are also suitable herein.

Bleach Catalyst

The compositions optionally contain a transition metal containing bleach catalyst. One suitable type of bleach catalyst is a catalyst system comprising a heavy metal cation of defined bleach catalytic activity, such as copper, iron or manganese cations, an auxiliary metal cation having little or no bleach catalytic activity, such as zinc or aluminum cations, and a sequestrant having defined stability constants for the catalytic and auxiliary metal cations, particularly ethylenediaminetetraacetic acid, ethylenediaminetetra(methylenephosphonic acid) and water-soluble salts thereof. Such catalysts are disclosed in U.S. Pat. 4,430,243.

Other types of bleach catalysts include the manganese-based complexes disclosed in U.S. Pat. 5,246,621 and U.S. Pat. 5,244,594. Preferred examples of these catalysts include Mn^{IV}₂(u-O)₃(1,4,7-trimethyl-1,4,7-triazacyclononane)₂-(PF₆)₂, Mn^{III}₂(u-O)₁(u-OAc)₂(1,4,7-trimethyl-1,4,7-triazacyclononane)₂-(ClO₄)₂, Mn^{IV}₄(u-O)₆(1,4,7-triazacyclononane)₄-(ClO₄)₂, Mn^{III}Mn^{IV}₄(u-O)₁(u-OAc)₂-

(1,4,7-trimethyl-1,4,7-triazacyclononane)₂-(ClO₄)₃, and mixtures thereof. Others are described in European patent application publication no. 549,272. Other ligands suitable for use herein include 1,5,9-trimethyl-1,5,9-triazacyclododecane, 2-methyl-1,4,7-triazacyclononane, 2-methyl-1,4,7-triazacyclononane, 1,2,4,7-tetramethyl-1,4,7-triazacyclononane, and mixtures thereof.

For examples of suitable bleach catalysts see U.S. Pat. 4,246,612 and U.S. Pat. 5,227,084. See also U.S. Pat. 5,194,416 which teaches mononuclear manganese (IV) complexes such as Mn(1,4,7-trimethyl-1,4,7-triazacyclononane)(OCH₃)₃-(PF₆). Still another type of bleach catalyst, as disclosed in U.S. Pat. 5,114,606, is a water-soluble complex of manganese (III), and/or (IV) with a ligand which is a non-carboxylate polyhydroxy compound having at least three consecutive C-OH groups. Other examples include binuclear Mn complexed with tetra-N-dentate and bi-N-dentate ligands, including N₄Mn^{III}(u-O)₂Mn^{IV}N₄)⁺ and [Bipy₂Mn^{III}(u-O)₂Mn^{IV}bipy₂](ClO₄)₃.

Further suitable bleach catalysts are described, for example, in European patent application No. 408,131 (cobalt complex catalysts), European patent applications, publication nos. 384,503, and 306,089 (metallo-porphyrin catalysts), U.S. 4,728,455 (manganese/multidentate ligand catalyst), U.S. 4,711,748 and European patent application, publication no. 224,952, (absorbed manganese on aluminosilicate catalyst), U.S. 4,601,845 (aluminosilicate support with manganese and zinc or magnesium salt), U.S. 4,626,373 (manganese/ligand catalyst), U.S. 4,119,557 (ferric complex catalyst), German Pat. specification 2,054,019 (cobalt chelant catalyst) Canadian 866,191 (transition metal-containing salts), U.S. 4,430,243 (chelants with manganese cations and non-catalytic metal cations), and U.S. 4,728,455 (manganese gluconate catalysts).

Heavy Metal Ion Sequestrant

The composition preferably contain as an optional component a heavy metal ion sequestrant. By heavy metal ion sequestrant it is meant herein components which act to sequester (chelate) heavy metal ions. These components may also have calcium and magnesium chelation capacity, but preferentially they show selectivity to binding heavy metal ions such as iron, manganese and copper. Heavy metal ion sequestrants are generally present at a level of from 0.005% to 20%, preferably from 0.1% to 10%, more preferably from 0.25% to 7.5% and most preferably from 0.5% to 5% by weight of the compositions or particle. Suitable heavy metal ion sequestrants for use herein

include organic phosphonates, such as the amino alkylene poly (alkylene phosphonates), alkali metal ethane 1-hydroxy disphosphonates and nitrilo trimethylene phosphonates.

Preferred among the above species are diethylene triamine penta (methylene phosphonate), ethylene diamine tri (methylene phosphonate) hexamethylene diamine tetra (methylene phosphonate) and hydroxy-ethylene 1,1 diphosphonate. Other suitable heavy metal ion sequestrant for use herein include nitrilotriacetic acid and polyaminocarboxylic acids such as ethylenediaminetetracetic acid, ethylenetriamine pentacetic acid, ethylenediamine disuccinic acid, ethylenediamine diglutamic acid, 2-hydroxypropylenediamine disuccinic acid or any salts thereof. Especially preferred is ethylenediamine-N,N'-disuccinic acid (EDDS) or the alkali metal, alkaline earth metal, ammonium, or substituted ammonium salts thereof, or mixtures thereof.

Other suitable heavy metal ion sequestrants for use herein are iminodiacetic acid derivatives such as 2-hydroxyethyl diacetic acid or glyceryl imino diacetic acid, described in EP-A-317,542 and EP-A-399,133. The iminodiacetic acid-N-2-hydroxypropyl sulfonic acid and aspartic acid N-carboxymethyl N-2-hydroxypropyl-3-sulfonic acid sequestrants described in EP-A-516,102 are also suitable herein. The β -alanine-N,N'-diacetic acid, aspartic acid-N,N'-diacetic acid, aspartic acid-N-monoacetic acid and iminodisuccinic acid sequestrants described in EP-A-509,382 are also suitable.

EP-A-476,257 describes suitable amino based sequestrants. EP-A-510,331 describes suitable sequestrants derived from collagen, keratin or casein. EP-A-528,859 describes a suitable alkyl iminodiacetic acid sequestrant. Dipicolinic acid and 2-phosphonobutane-1,2,4-tricarboxylic acid are also suitable. Glycinamide-N,N'-disuccinic acid (GADS), ethylenediamine-N,N'-diglutamic acid (EDDG) and 2-hydroxypropylenediamine-N,N'-disuccinic acid (HPDDDS) are also suitable.

Enzyme

Another preferred ingredient useful in the composition is one or more additional enzymes. Preferred additional enzymatic materials include the commercially available lipases, cutinases, amylases, neutral and alkaline proteases, esterases, cellulases, pectinases, lactases and peroxidases conventionally incorporated into detergent compositions. Suitable enzymes are

discussed in US Patents 3,519,570 and 3,533,139. Preferred commercially available protease enzymes include those sold under the tradenames Alcalase, Savinase, Primase, Durazym, and Esperase by Novo Industries A/S (Denmark), those sold under the tradename Maxatase, Maxacal and Maxapem by Gist-Brocades, those sold by Genencor International, and those sold under the tradename Opticlean and Optimase by Solvay Enzymes. Protease enzyme may be incorporated into the compositions in accordance with the invention at a level of from 0.0001% to 4% active enzyme by weight of the composition.

Preferred amylases include, for example, α -amylases obtained from a special strain of *B licheniformis*, described in more detail in GB-1,269,839 (Novo). Preferred commercially available amylases include for example, those sold under the tradename Rapidase by Gist-Brocades, and those sold under the tradename Termamyl and BAN by Novo Industries A/S. Amylase enzyme may be incorporated into the composition in accordance with the invention at a level of from 0.0001% to 2% active enzyme by weight of the composition.

Lipolytic enzyme may be present at levels of active lipolytic enzyme of from 0.0001% to 10% by weight of the particle, preferably 0.001% to 3% by weight of the composition, most preferably from 0.001% to 0.5% by weight of the compositions.

The lipase may be fungal or bacterial in origin being obtained, for example, from a lipase producing strain of *Humicola* sp., *Thermomyces* sp. or *Pseudomonas* sp. including *Pseudomonas pseudoalcaligenes* or *Pseudomonas fluorescens*. Lipase from chemically or genetically modified mutants of these strains are also useful herein. A preferred lipase is derived from *Pseudomonas pseudoalcaligenes*, which is described in Granted European Patent, EP-B-0218272.

Another preferred lipase herein is obtained by cloning the gene from *Humicola lanuginosa* and expressing the gene in *Aspergillus oryza*, as host, as described in European Patent Application, EP-A-0258 068, which is commercially available from Novo Industri A/S, Bagsvaerd, Denmark, under the trade name Lipolase. This lipase is also described in U.S. Patent 4,810,414, Høge-Jensen et al, issued March 7, 1989.

Organic Polymeric Compound

Organic polymeric compounds are preferred in compositions. By organic polymeric compound it is meant herein essentially any polymeric organic

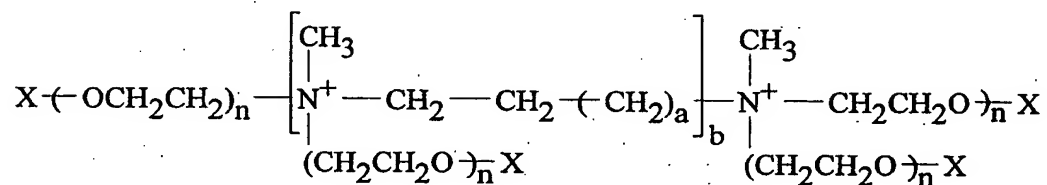
compound commonly used as dispersants, and anti-redeposition and soil suspension agents in detergent compositions, including any of the high molecular weight organic polymeric compounds described as clay flocculating agents herein.

5 Organic polymeric compound is typically incorporated in the detergent compositions of the invention at a level of from 0.1% to 50% by weight of the particle, preferably from 0.5% to 25%, most preferably from 1% to 15% by weight of the compositions.

10 Examples of organic polymeric compounds include the water soluble organic homo- or co-polymeric polycarboxylic acids or their salts in which the polycarboxylic acid comprises at least two carboxyl radicals separated from each other by not more than two carbon atoms. Polymers of the latter type are disclosed in GB-A-1,596,756. Examples of such salts are polyacrylates of MWt 2000-5000 and their copolymers with maleic anhydride, such copolymers having 15 a molecular weight of from 20,000 to 100,000, especially 40,000 to 80,000. The polyamino compounds are useful herein including those derived from aspartic acid such as those disclosed in EP-A-305282, EP-A-305283 and EP-A-351629.

20 Terpolymers containing monomer units selected from maleic acid, acrylic acid, polyaspartic acid and vinyl alcohol, particularly those having an average molecular weight of from 5,000 to 10,000, are also suitable herein. Other organic polymeric compounds suitable for incorporation in the detergent compositions herein include cellulose derivatives such as methylcellulose, carboxymethylcellulose, hydroxypropylmethylcellulose and hydroxyethylcellulose.

25 Another organic compound, which is a preferred clay dispersant/ anti-redeposition agent, for use herein, can be the ethoxylated cationic monoamines and diamines of the formula:



30 wherein X is a nonionic group selected from the group consisting of H, C₁-C₄ alkyl or hydroxyalkyl ester or ether groups, and mixtures thereof, a is from 0 to

20, preferably from 0 to 4 (e.g. ethylene, propylene, hexamethylene) b is 1 or 0; for cationic monoamines (b=0), n is at least 16, with a typical range of from 20 to 35; for cationic diamines (b=1), n is at least about 12 with a typical range of from about 12 to about 42.

5 Other dispersants/ anti-redeposition agents for use herein are described in EP-B-011965 and US 4,659,802 and US 4,664,848.

Clay Softening System

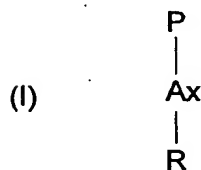
The compositions may contain a clay softening system comprising a clay mineral compound and optionally a clay flocculating agent. The clay mineral compound is
10 preferably a smectite clay compound. Smectite clays are disclosed in the US Patents No.s 3,862,058, 3,948,790, 3,954,632 and 4,062,647. European Patents No.s EP-A-299,575 and EP-A-313,146 in the name of the Procter and Gamble Company describe suitable organic polymeric clay flocculating agents.

Polymeric Dye Transfer Inhibiting Agents

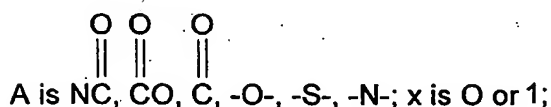
15 The particles or compositions herein may also comprise from 0.01% to 10 %, preferably from 0.05% to 0.5% by weight of polymeric dye transfer inhibiting agents. The polymeric dye transfer inhibiting agents are preferably selected from polyamine N-oxide polymers, copolymers of N-vinylpyrrolidone and N-vinylimidazole, polyvinylpyrrolidone polymers or combinations thereof.

a) Polyamine N-oxide polymers

20 Polyamine N-oxide polymers suitable for use herein contain units having the following structure formula :



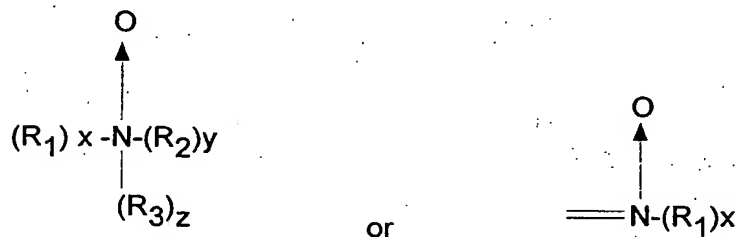
25 wherein P is a polymerisable unit, and



R are aliphatic, ethoxylated aliphatics, aromatic, heterocyclic or alicyclic groups or any combination thereof whereto the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group is part of these groups.

The N-O group can be represented by the following general

5 structures :



10 wherein R₁, R₂, and R₃ are aliphatic groups, aromatic, heterocyclic or alicyclic groups or combinations thereof, x or/and y or/and z is 0 or 1 and wherein the nitrogen of the N-O group can be attached or wherein the nitrogen of the N-O group forms part of these groups. The N-O group can be part of the polymerisable unit (P) or can be attached to the polymeric backbone or a combination of both.

15 Suitable polyamine N-oxides wherein the N-O group forms part of the polymerisable unit comprise polyamine N-oxides wherein R is selected from aliphatic, aromatic, alicyclic or heterocyclic groups. One class of said polyamine N-oxides comprises the group of polyamine N-oxides wherein the nitrogen of the N-O group forms part of the R-group. Preferred polyamine N-oxides are those
 20 wherein R is a heterocyclic group such as pyridine, pyrrole, imidazole, pyrrolidine, piperidine, quinoline, acridine and derivatives thereof.

Other suitable polyamine N-oxides are the polyamine oxides whereto the N-O group is attached to the polymerisable unit. A preferred class of these polyamine N-oxides comprises the polyamine N-oxides having the general
 25 formula (I) wherein R is an aromatic, heterocyclic or alicyclic groups wherein the nitrogen of the N-O functional group is part of said R group. Examples of these classes are polyamine oxides wherein R is a heterocyclic compound such as pyridine, pyrrole, imidazole and derivatives thereof.

The polyamine N-oxides can be obtained in almost any degree of
 30 polymerisation. The degree of polymerisation is not critical provided the material

has the desired water-solubility and dye-suspending power. Typically, the average molecular weight is within the range of 500 to 1000,000.

b) Copolymers of N-vinylpyrrolidone and N-vinylimidazole

Suitable herein are copolymers of N-vinylimidazole and N-vinylpyrrolidone having an average molecular weight range of from 5,000 to 50,000. The preferred copolymers have a molar ratio of N-vinylimidazole to N-vinylpyrrolidone from 1 to 0.2.

c) Polyvinylpyrrolidone

The compositions herein may also utilize polyvinylpyrrolidone ("PVP") having an average molecular weight of from 2,500 to 400,000. Suitable polyvinylpyrrolidones are commercially available from ISP Corporation, New York, NY and Montreal, Canada under the product names PVP K-15 (viscosity molecular weight of 10,000), PVP K-30 (average molecular weight of 40,000), PVP K-60 (average molecular weight of 160,000), and PVP K-90 (average molecular weight of 360,000). PVP K-15 is also available from ISP Corporation. Other suitable polyvinylpyrrolidones which are commercially available from BASF Cooperation include Sokalan HP 165 and Sokalan HP 12.

d) Polyvinylloxazolidone

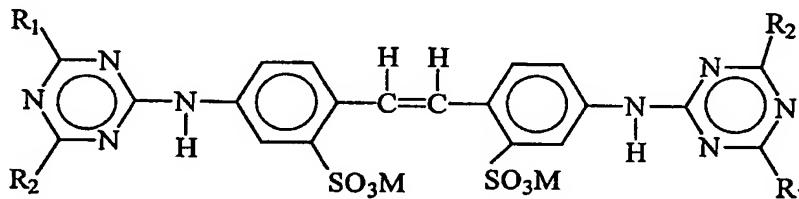
The compositions herein may also utilize polyvinylloxazolidones as polymeric dye transfer inhibiting agents. Said polyvinylloxazolidones have an average molecular weight of from 2,500 to 400,000.

e) Polyvinylimidazole

The compositions herein may also utilize polyvinylimidazole as polymeric dye transfer inhibiting agent. Said polyvinylimidazoles preferably have an average molecular weight of from 2,500 to 400,000.

Optical Brightener

The compositions herein also optionally contain from about 0.005% to 5% by weight of certain types of hydrophilic optical brighteners. Hydrophilic optical brighteners useful herein include those having the structural formula:



wherein R₁ is selected from anilino, N-2-bis-hydroxyethyl and NH-2-hydroxyethyl; R₂ is selected from N-2-bis-hydroxyethyl, N-2-hydroxyethyl-N-methylamino, morphilino, chloro and amino; and M is a salt-forming cation such as sodium or potassium.

When in the above formula, R₁ is anilino, R₂ is N-2-bis-hydroxyethyl and M is a cation such as sodium, the brightener is 4,4',-bis[(4-anilino-6-(N-2-bis-hydroxyethyl)-s-triazine-2-yl)amino]-2,2'-stilbenedisulfonic acid and disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal-UNPA-GX by Ciba-Geigy Corporation. Tinopal-UNPA-GX is the preferred hydrophilic optical brightener useful in the detergent compositions herein. When in the above formula, R₁ is anilino, R₂ is N-2-hydroxyethyl-N-2-methylamino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-(N-2-hydroxyethyl-N-methylamino)-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid disodium salt. This particular brightener species is commercially marketed under the tradename Tinopal 5BM-GX by Ciba-Geigy Corporation. When in the above formula, R₁ is anilino, R₂ is morphilino and M is a cation such as sodium, the brightener is 4,4'-bis[(4-anilino-6-morphilino-s-triazine-2-yl)amino]2,2'-stilbenedisulfonic acid, sodium salt. This particular brightener species is commercially marketed under the tradename Tinopal AMS-GX by Ciba Geigy Corporation.

Cationic Fabric Softening Agents

Cationic fabric softening agents can also be incorporated into compositions in accordance with the present invention. Suitable cationic fabric softening agents include the water insoluble tertiary amines or dilong chain amide materials as disclosed in GB-A-1 514 276 and EP-B-0 011 340. Cationic fabric softening agents are typically incorporated at total levels of from 0.5% to 15% by weight, normally from 1% to 5% by weight.

pH of the Compositions

The detergent compositions preferably can have an acidic or an alkaline pH, depending on the application or the additional ingredients. It may be preferred that the particles or the compositions have a pH, measured as a 1% solution in distilled water, of at least 3.0, preferably from 4.0 to 12.5.

D. Laundry Methods

In a manual laundry method, the method typically comprises contacting and/or treating soiled fabric with an aqueous wash solution containing detergent composition in a bucket or a container with a solid bar. The consumer contacts the solid bar with the soiled fabric by scrubbing. After all the fabric has been scrubbed, fresh water is added to the container and the fabrics are rinsed. This rinsing process may be repeated. During a typical manual laundry method, a cleaning or scrubbing implement may also be used.

In a machine laundry method, the method typically comprises treating soiled laundry with an aqueous wash solution containing detergent composition having dissolved or dispensed therein an effective amount of detergent composition. Preferably, an effective amount is from about 10g to about 300 g or product dissolved or dispersed in a wash solution of volume from about 5 to 65 litres.

In a method or soaking fabrics, soiled fabrics are immersed in an aqueous soaking solution containing detergent composition for an effective period of time. Then, the fabrics are removed from the soaking solution.

EXAMPLES

The following examples further describe and demonstrate embodiments within the scope of the present invention. The examples are given solely for the purpose of illustration and are not to be construed as limitations of the present invention, as many variations thereof are possible without departing from the spirit and scope of the invention.

In the following Examples all levels are quoted as % by weight of the composition. The following examples are illustrative of the present invention, but are not meant to limit or otherwise define its scope. All parts, percentages and ratios used herein are expressed as percent weight unless otherwise specified.

Abbreviations used in Examples

In the exemplified foaming systems and cleaning compositions, the abbreviated component identifications have the following meanings:

LAS	:	Sodium linear C ₁₂ alkyl benzene sulfonate
TAS	:	Sodium tallow alkyl sulfate
C45AS	:	Sodium C ₁₄ -C ₁₅ linear alkyl sulfate
MES	:	α -sulpho methylester of C ₁₈ fatty acid

	CxyEzS	:	Sodium C _{1x} -C _{1y} branched alkyl sulfate condensed with z moles of ethylene oxide
	MBAS _{x, y}	:	Sodium mid-chain branched alkyl sulfate having an average of x carbon atoms, whereof an average of y carbons comprised in (a) branching unit(s)
5			
	C48 SAS	:	Sodium C ₁₄ -C ₁₈ secondary alcohol sulfate
	SADExS	:	Sodium C ₁₄ -C ₂₂ alkyl disulfate of formula 2-(R).C ₄ H ₇ -1,4-(SO ₄ -) ₂ where R = C ₁₀ C ₁₈ , condensed with
10			z moles of ethylene oxide
	CxyEz	:	A C _{1x-1y} branched primary alcohol condensed with an average of z moles of ethylene oxide
	QAS I	:	R ₂ .N ⁺ (CH ₃) ₂ (C ₂ H ₄ OH) with R ₂ = 50%-60% C ₉ ; 40%-50% C ₁₁
15	QAS II	:	R ₁ .N ⁺ (CH ₃)(C ₂ H ₄ OH) ₂ with R ₁ = C ₁₂ -C ₁₄
	Soap	:	Sodium linear alkyl carboxylate derived from an 80/20 mixture of tallow and coconut oils.
	TFAA I	:	C ₁₂ -C ₁₄ alkyl N-methyl glucamide
	TFAA II	:	C ₁₆ -C ₁₈ alkyl N-methyl glucamide
20	TPKFA	:	C ₁₂ -C ₁₄ topped whole cut fatty acids
	STPP	:	Anhydrous sodium tripolyphosphate
	Zeolite A I	:	Hydrated Sodium Aluminosilicate of formula Na ₁₂ (Al ₁₀ Si ₂ O ₂) ₁₂ . 27H ₂ O having a primary particle size in the range from 0.1 to 10 micrometers
25	Zeolite A II	:	overdried Zeolite A I
	NaSKS-6	:	Crystalline layered silicate of formula δ -Na ₂ Si ₂ O ₅
	Citric acid I	:	Anhydrous citric acid
	Citric acid II	:	Citric acid monohydrate
	Malic acid	:	Anhydrous malic acid
30	Maleic acid	:	Anhydrous maleic acid
	Aspartic acid	:	Anhydrous aspartic acid
	Carbonate I	:	Anhydrous sodium carbonate with an average particle size between 200μm and 900μm
35	Carbonate II	:	Anhydrous sodium carbonate with an average particle size between 100μm and 200μm

	Bicarbonate	:	Anhydrous sodium bicarbonate with a particle size distribution between 400µm and 1200µm
	Silicate	:	Amorphous Sodium Silicate (SiO ₂ :Na ₂ O; 2.0 ratio)
	Sodium sulfate	:	Anhydrous sodium sulfate
5	Citrate	:	Tri-sodium citrate dihydrate of activity 86.4% with a particle size distribution between 425µm and q 850µm
	MA/AA	:	Copolymer of 1:4 maleic/acrylic acid, average molecular weight about 70,000
	CMC	:	Sodium carboxymethyl cellulose
10	Protease	:	Proteolytic enzyme of activity 4KNPU/g sold by NOVO Industries A/S under the tradename Savinase
	Alcalase	:	Proteolytic enzyme of activity 3AU/g sold by NOVO Industries A/S
	Cellulase	:	Cellulytic enzyme of activity 1000 CEVU/g sold by
15	Amylase	:	NOVO Industries A/S under the tradename Carezyme
	Amylase	:	Amylolytic enzyme of activity 60KNU/g sold by NOVO Industries A/S under the tradename Termamyl 60T
	Lipase	:	Lipolytic enzyme of activity 100kLU/g sold by NOVO Industries A/S under the tradename Lipolase
20	Endolase	:	Endoglunase enzyme of activity 3000 CEVU/g sold by NOVO Industries A/S
	PB4	:	Sodium perborate tetrahydrate of nominal formula NaBO ₂ .3H ₂ O.H ₂ O ₂
	PB1	:	Anhydrous sodium perborate bleach of nominal
25	Percarbonate	:	formula NaBO ₂ .H ₂ O ₂
	Percarbonate	:	Sodium Percarbonate of nominal formula 2Na ₂ CO ₃ .3H ₂ O ₂
	NAC-OBS	:	(Nonanamido caproyl) oxybenzene sulfonate in the form of the sodium salt.
30	NOBS	:	Nonanoyl oxybenzene sulfonate in the form of the sodium salt
	DPDA	:	Diperoxydodecanedioic acid
	PAP	:	N-phthaloylamidoperoxicaproic acid
	NAPAA	:	Nonanoylamido peroxo-adipic acid
35	NACA	:	6 nonylamino - 6 oxo - capronic acid.

	TAED	:	Tetraacetythylenediamine
	DTPMP	:	Diethylene triamine penta (methylene phosphonate), marketed by Monsanto under the Trade name Dequest 2060
5	Photoactivated	:	Sulfonated Zinc or aluminium Phthlocyanine encapsulated
	Brightener 1	:	Disodium 4,4'-bis(2-sulphostyryl)biphenyl
	Brightener 2	:	Disodium 4,4'-bis(4-anilino-6-morpholino-1.3.5-triazin-2-yl)amino) stilbene-2:2'-disulfonate.
10	HEDP	:	1,1-hydroxyethane diphosphonic acid
	PVNO	:	Polyvinylpyridine N-oxide
	PVPVI	:	Copolymer of polyvinylpyrrolidone and vinylimidazole
	QEA	:	bis ((C ₂ H ₅ O)(C ₂ H ₄ O) _n) (CH ₃) -N ⁺ -C ₆ H ₁₂ -N ⁺ - (CH ₃) bis ((C ₂ H ₅ O)-(C ₂ H ₄ O) _n), wherein n=from 20 to 30
15	SRP 1	:	Sulfobenzoyl end capped esters with oxyethylene oxy and terephthaloyl backbone
	SRP 2	:	Diethoxylated poly (1, 2 propylene terephthalate) short block polymer
20	Delayed-release foam suppressing comp. 1	:	A flake material containing about 10%, by weight, of silicone/silica fluid and 90% by weight, of polyethylene glycol having a molecular weight of about 8,000. The flake material has a particle size of 2000 microns to about 500 microns (-10/+35 Tyler mesh).
25	Delayed-release foam suppressing comp. 2	:	A flake material containing about 10% by weight of silicone/silica fluid, about 0 to 7% by weight of palmitic acid or Hyfac® fatty acids, and the balance polyethylene glycol having a molecular weight of about 8,000. The flake material has a particle size of 2000 microns to about 500 microns (-10/+35 Tyler mesh).
30	Suds Booster:	:	One or a mixture of polyethylene glycol, amine oxide, monoethanol amine, diethanol amine, fatty alcohol, sugar, protein and betaine.

In the following Examples all levels are quoted as parts per weight of the composition:

Controlled Foaming System Examples

5

The following examples exemplify foaming systems in accord with the invention, each of which, or mixtures thereof, can be used in detergent compositions.

10 The controlled foaming system of the present invention can be made by any method known in the art for formation of particles, as described above.

15 In the foaming system, there are many variations of how the foaming component and the delayed-release foam suppressing component may be combined. For example, the foaming component and the foam suppressing component may be agglomerated or otherwise mixed together with other optional components to form one solid particle. In addition, the foaming component and the foam suppressing component may be two separate particles. Either the one solid particle or the two separate particles making up the foaming system may be used in detergent compositions.

Example 1**Foaming Systems A to J**

	A	B	C	D	E	F	G	H	I	J
TFAA I/ TFAAII	31.0	28.0	11.0	27.5	13.0	15.0	22.0	15.0	-	10.0
C24E3/ C24E5	-	-	28.0	-	25.0	22.0	-	5.0	10.0	10.0
PEG 4000	5.0	5.3	-	5.0	-	-	7.0	5.0	-	5.0
citric acid I	13.5	14.0	20.0	15.5	16.0	15.0	15.0	10.0	-	10.0
Maleic acid	-	-	-	-	-	-	-	-	10.5	10.0
sodium carbonate I	13.5	-	20.0	-	-	-	-	-	15.0	10.0
sodium carbonate II	-	14.0	-	6.0	14.0	10.0	10.0	10.0	5.0	-
sodium bicarbonate	-	-	-	6.0	-	-	10.0	-	5.5	5.0
Zeolite A II	18.0	35.7	20.0	18.0	-	9.0	10.0	5.0	14.0	17.0
LAS	9.0	-	-	-	12.0	-	-	10.0	-	13.0
QAS I/ QAS II	9.0	-	-	-	-	-	6.0	3.0	-	-
TAED/ NOBS/ NACA-OBS	-	-	-	19.0	10.0	-	-	7.0	20.0	-
Perborate/ percarbonate	-	-	-	-	-	19.0	-	10.0	-	-
Foam supp. Component 1	1.0	3.0	-	-	10.0	-	10.0	-	-	5.0
Foam supp. Component 2	-	-	1.0	3.0	-	10.0	-	10.0	10.0	5.0
Suds Booster	-	-	-	-	-	-	10.0	10.0	10.0	-

5 Foaming systems A-J produces upon contact with water gas bubbles having an average bubble particle size of about 400 microns or less, and the foam suppressing components reduces the water gas bubbles as soon as the mixture is agitated. The bubbles have been reduced at least about 40% to about 70% after about 6 to 10 minutes after the mixture is first agitated.

The following examples exemplify cleaning compositions comprising the foaming component of the invention:

Example 2

10 The following are high density and bleach-containing detergent formulations according to the present invention (can be for either granular form or tablet form):

	a	b	c
Blown Powder			
Zeolite A	5.0	5.0	15.0
Sodium sulfate	0.0	5.0	0.0
LAS	20.0	30.0	20.0
C45AS	3.0	5.0	20.0
QAS	-	-	1.5
DTPMP	0.4	0.4	0.4
CMC	0.4	0.4	0.4
MA/AA	4.0	2.0	2.0
Foaming System A	20.0		
Foaming System B	-	15.0	-
Foaming System G	-	-	10.0
Spray On (on particles)			
Encapsulated Perfume	0.3	0.3	0.3
C25E3	-	-	2.0
Dry additives			
QEA	-	-	0.5
Citrate	5.0	-	2.0
Bicarbonate	-	3.0	-

Carbonate	8.0	10.0	5.0
NAC OBS	6.0	-	-
Manganese catalyst	-	-	0.3
NOBS	-	2.0	-
PB1	14.0	7.0	-
Polyethylene oxide of MW 5,000,000	-	-	0.2
Bentonite clay	-	-	10.0
Citric acid	-	-	0.5
Protease	1.0	1.0	1.0
Lipase	0.4	0.4	0.4
Amylase	0.6	0.6	0.6
Cellulase	0.6	0.6	0.6
Suds Booster	5.0	1.0	5.0
Dry additives			
Sodium sulfate	0.0	3.0	0.0
Balance (Moisture and Miscellaneous)	100.0	100.0	100.0
Density (g/litre)	750	800	700

Example 3

The following are high density detergent formulations according to the present invention:

5

	d	e
Foaming System A	45.0	
Foaming System H		60.0
Spray On		
C25E3	-	1.0
Perfume	0.5	0.5
Dry Adds		
HEDP	0.5	0.3
SKS 6	13.0	10.0
Citrate	-	1.0
NAC OBS	4.1	-
TAED	0.8	-
Percarbonate	20.0	5.0
SRP 1	0.3	0.3
Protease	1.4	1.4
Lipase	0.4	0.4
Cellulase	0.6	0.6
Amylase	0.6	0.6
QEA	1.0	-
Suds Booster	5.0	-
Brightener 1	0.2	0.2
Brightener 2	0.2	-
Density (g/litre)	700	850

It is understood that the examples and embodiments described herein are for illustrative purposes only and that various modifications or changes in light thereof will be suggested to one skilled in the art without departing from its spirit and scope.

10

WHAT IS CLAIMED IS:

1. A controlled foaming system especially adapted for use in detergent compositions comprising:
 - (a) a foaming component capable of providing foaming or sudsing without agitation; and
 - 5 (b) a delayed-release foam suppressing component.
2. The controlled foaming system of Claim 1, wherein the foaming component comprises an effervescent granule comprising an acid source, and carbonate and/or bicarbonate.
3. The controlled foaming system of Claim 2, wherein the delayed-release foam suppressing component is a silicone foam suppressing agent which is releasably incorporated in a carrier, thereby delaying the release of a silicone foam suppressing agent.
4. The controlled foaming system of Claim 3, wherein the silicone foam suppressing agent has an average droplet diameter of from about 1 to about 50 microns releasably incorporated in a water-soluble or water dispersible, substantially non-surface active, detergent-impermeable, and non-
5 hydroscopic carrier, the silicone foam suppressing component being substantially free of water-soluble relatively hydroscopic inorganic salts and in the form of an irregularly shaped particle having a minimum dimension of not less than about 0.05 cm and the maximum dimension being at least about 20% greater than the minimum dimension.
5. The controlled foaming system of Claim 2, wherein the foaming component produces upon contact with water gas bubbles having an average bubble particle size of about 400 microns or less, preferably about 200 microns or less, and more preferably about 100 microns or less.
6. The controlled foaming system of Claim 2, wherein the acid source is selected from acids and hydrated or anhydrous salts of acids and is a mono or polycarboxylic acid selected from the group consisting of citric, malic, maleic, fumaric aspartic, glutaric, tartaric, malonic, succinic or adipic acid,
5 monosodium phosphate, boric acid, 3 chetoglutaric acid, citramalic acid, and mixtures thereof.
7. The controlled foaming system of Claim 2, wherein the effervescent granule further comprises a binder selected from the group consisting of cellulose

- derivatives, carboxymethylcellulose and homo- and co- polymeric polycarboxylic acid and their salts, C6-C20 alkyl and alkylaryl sulphonates and sulphates, C10-C20 alcohol ethoxylates containing from about 5 to about 100 moles of ethylene oxide per mole of alcohol, polyvinylpyrrolidones with an average molecular weight of from about 12 000 to about 700 000, polyethylene glycols with an average weight of from about 600 to about 10 000, copolymers of maleic anhydride with ethylene, methylvinyl ether, methacrylic acid or acrylic acid, C10-C20 mono and diglycerol ethers, C10-C20 fatty acids and mixtures thereof.
- 5
- 10
8. The controlled foaming system of Claim 4, wherein the non-hydroscopic carrier is a polyethylene glycol carrier, the carrier further comprising from about 0.2% to about 15% fatty acid or soap having from about 10 to about 30 carbon atoms, and/or wax.
 9. The controlled foaming system of Claim 2, wherein the delayed-release foaming component further comprises a suds booster selected from the group consisting of amine oxide, polyethylene glycol, monoethanol amine, diethanol amine, fatty alcohol, sugar, protein, betaine, and mixtures thereof.
 10. The controlled foaming system of Claim 2, wherein the foaming component and the delayed-release foam suppressing component are independent dry particles, wherein the foaming component has an average particle size of from about 75 microns to about 2 cm.
 11. A granular detergent composition comprising the controlled foaming system of Claim 1, further comprising a deterative component selected from the group consisting of surfactants, bleaches, alkali metal salt of silicate, builders, chelating agents, enzymes, fillers, soil suspending agents, optical brighteners, dispersants, soil release agents, photoactivated bleaches, dyes, dye transfer inhibitors, pigments, perfumes, clay softening system, cationic fabric softening agents, and mixtures thereof.
 12. A method of cleaning and soaking fabrics, comprising contacting the fabric in a solution containing water and the granular detergent composition of Claim 11 for an effective period of time for a time sufficient to clean said fabric.
- 5

Internal Application No. PCT/US 98/0020

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C11D3/37 C11D17/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C11D B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 93 01269 A (UNILEVER) 21 January 1993	1-3,5-7,
A	see page 6, line 16 - line 21; claim 1; example 5; table 4	11,12 4,8-10
A	WO 98 04661 A (PROCTER & GAMBLE) 5 February 1998 see page 28, line 19 - page 30, line 29; claims 1,13,18; example 1	1-8,11, 12
A	EP 0 206 522 A (UNILEVER) 30 December 1986 see claims 1-15	1,3,4, 7-12
A	EP 0 336 710 A (DOW CORNING) 11 October 1989 see claim 1; example 2	1,3,4,7, 11,12

-/-

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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INTERNATIONAL SEARCH REPORT

Inter: al App No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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